

Relationship between the Composition of Polycarbonate Copolymers and the Refractive Index

MASAYA OKAMOTO

Polymer Research Laboratory, Idemitsu Petrochemical Company, Limited, 1-1 Anesaki-Kaigan, Ichihara, Chiba, 299-0193, Japan

Received 19 December 2000; accepted 10 July 2001

ABSTRACT: With a polycarbonate (PC)–poly(methyl methacrylate) (PMMA) graft copolymer and a PC–poly(dimethyl siloxane) (PDMS) block copolymer, the relationship between the composition of PC copolymers and the refractive index (n_D) was investigated. According to the results, with a PMMA content of 38 wt %, the n_D value of the PC–PMMA graft copolymer was nearly the same as that of electrical (E) glass ($n_D = 1.545$), and with a PMMA content of 6 wt %, it was nearly the same as that of electrical corrosion resistance (ECR) glass ($n_D = 1.579$). However, with a PDMS content of 19 wt %, the n_D value of the PC–PDMS block copolymer was nearly the same as that of E glass, and with a PDMS content of 2 wt %, it was nearly the same as that of ECR glass. The combination of the PC–PDMS block copolymer and the glass fibers (GFs) of ECR glass led to haze values of 8 and 16% with GF contents of 10 and 20%, respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 514–521, 2002; DOI 10.1002/app.2355

Key words: polycarbonates; poly(methyl methacrylate); poly(dimethyl siloxane); refractive index; transparency

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics because of their good impact strength, thermal resistance, and transparency.^{1,2} They are used as base resins of fibrous, glass-reinforced plastics [glass-fiber polycarbonates (GFPCs)] that are superior in rigidity and dimensional stability but inferior in transparency. Their poor transparency is due to a significant difference in the refractive index (n_D) between the PCs and the glass fibers (GFs); that is, the n_D value of PCs is approximately 1.585, and that of electrical (E) glass used for GFPCs is approximately 1.545. Recently, electrical corrosion resistance (ECR) glass with a superior corrosion

resistant property and a high value of n_D has been reported.³ Its n_D value is 1.579, which is not satisfactory for GFPCs. The development of GFPCs with high transparency as found in the PC base resins is desired for use as substitute glasses.

Among the latest studies on GFPCs, some articles report recycling by compression molding.^{4,5} Other articles report specific pigments that keep the toughness of GFPCs.^{6,7} However, no report deals with improving the transparency of GFPCs.

This article describes the n_D values of a PC–poly(methyl methacrylate) (PMMA)⁸ graft copolymer and a PC–poly(dimethyl siloxane) (PDMS) block copolymer that have the potential for improving the transparency of GFPCs.

EXPERIMENTAL

Materials

Commercial methyl methacrylate (MMA) and tetrahydrofuran (THF) were distilled *in vacuo*.

Correspondence to: M. Okamoto (masaya.okamoto@ipc.idemitsu.co.jp).

Journal of Applied Polymer Science, Vol. 84, 514–521 (2002)
© 2002 John Wiley & Sons, Inc.

α,α' -Azobisisobutyronitrile (AIBN) was recrystallized from commercial methanol. Commercial thiomalic acid (TMA), bisphenol A (BPA), *p*-tert-butylphenol (PTBP), triethylamine (TEA), octamethylcyclotetrasiloxane (OMTS), 1,1,3,3-tetramethylidisiloxane (TMDS), 2-allylphenol, sodium hydroxide, sodium hydrogen carbonate dichloromethane, petroleum ether, acetone, ethanol, and sodium dithionite were used without further purification. GFs of E glass (E-GF) and ECR-glass (ECR-GF) were supplied by Asahi Fiber Glass Co., Ltd. (Tokyo, Japan).

Preparation of the PC Oligomer

Sodium dithionite (120 g, 0.69 mol) and BPA (60 kg, 263 mol) were dissolved in 5 wt % aqueous sodium hydroxide (400 L). This solution, dichloromethane, and phosgene were introduced through an orifice plate at 25°C with flow rates of 138 L/h, 69 L/h, and 10.7 kg/h (108 mol/h), respectively, into a tubular reactor with an inner diameter of 10 mm and a length of 10 m. This procedure was continued for 3 h. Because phosgene is a toxic, irritating gas, it was handled only in an efficient fume hood. After the reaction solution was allowed to stand for a certain time, the organic phase was separated to obtain a PC oligomer solution with an oligomer concentration of 311 g/L and a chloroformate (CF) group concentration of 0.72 mol/L.

Preparation of the PMMA Macromonomer

A solution prepared by the dissolution of MMA (200 g, 1.998 mol), AIBN (2.296 g, 0.0014 mol), and TMA (17.72 g, 0.118 mol) in THF (400 mL) was heated at 60°C for 2.5 h.^{9,10} The resulting solution was poured into petroleum ether (4 L), and the precipitate obtained was filtered out and dried. The precipitate was then dissolved in dichloromethane and washed with water until the aqueous layer became neutral. By evaporation of the solvent, a PMMA macromonomer was obtained in a flake form. Its carboxyl group (COOH) content was determined by titration of the polymer in methanol with aqueous potassium hydroxide and with phenolphthalein as an indicator.

Preparation of the PC-PMMA Graft Copolymer

The PC oligomer solution was evaporated to obtain the oligomer in a flake form. TEA (1.81 mL, 12.98 mmol) was added to a solution prepared by the dissolution of the PC oligomer (60 g; CF, 129.2

mmol) and the PMMA macromonomer (18.46 g; COOH, 12.98 mmol) in dichloromethane (300 mL). The solution was stirred at room temperature for 1 h and washed with 0.1M aqueous hydrochloric acid, and the organic phase was then separated.

A solution prepared by the dissolution of PTBP (1.03 g, 6.86 mmol) in dichloromethane (30 mL) was added to this organic phase for use as an organic solvent in the following reaction. Separately, a solution was prepared by the dissolution of sodium dithionite (20 mg, 0.11 mmol), BPA (10.67 g, 46.74 mmol), sodium hydroxide (6.54 g, 163.5 mmol), and TEA (0.072 mL, 0.516 mmol) in water (110 mL). This solution, mixed with the aforementioned organic solvent, was subjected to interfacial polycondensation at 500 rpm and 23°C for 2 h. Dichloromethane (1 L) was then added to the resulting solution, which was washed successively with water (1 L), 0.01M aqueous sodium hydroxide (500 mL), 0.1M aqueous hydrochloric acid (500 mL), and water (500 mL). After the washing, the solvent was evaporated. The remaining polymer was extracted with acetone with a Soxhlet extractor to obtain a pure graft copolymer.

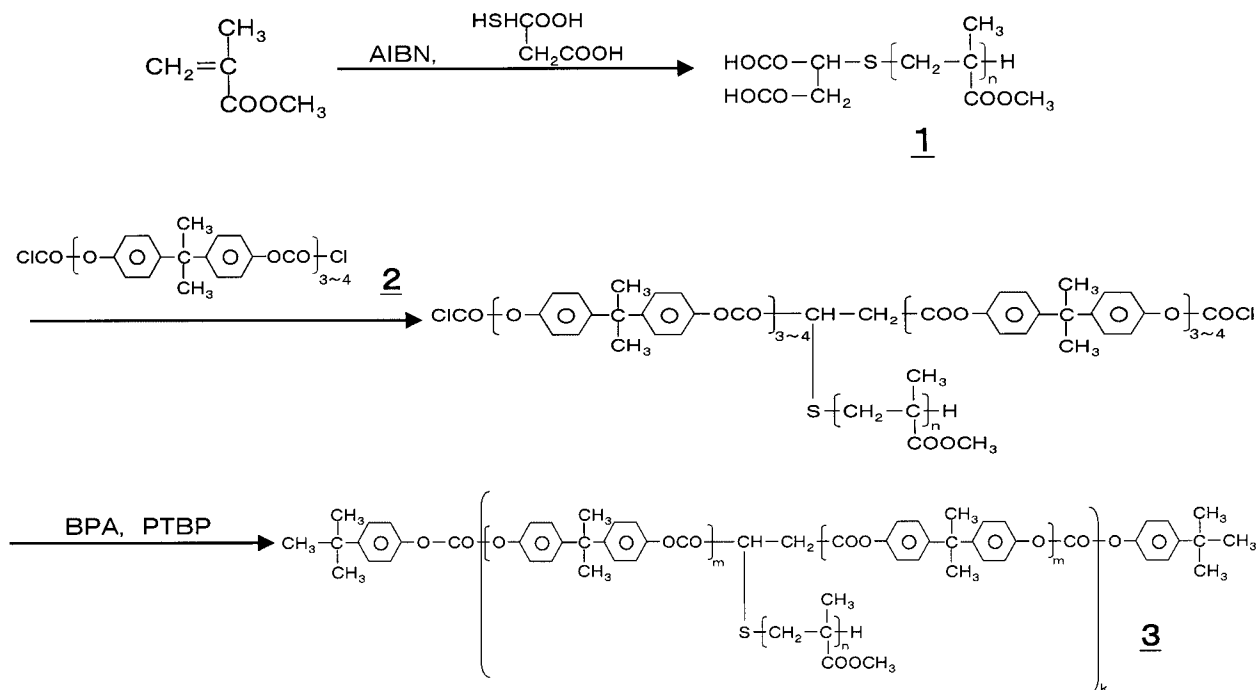
The resulting copolymer was dried for 12 h at 110°C and press-molded with mirror-finished aluminum sheets at 290°C, and the resulting molding was subjected to n_D measurements.

Preparation of the Reactive PDMS

A mixture of OMTS (1483 g, 5.0 mol), TMDS (74.69 g, 0.556 mol), and 35% aqueous sulfuric acid (35 g) was stirred at room temperature for 17 h.¹¹ After the acid layer was carefully separated, the oily layer was stirred with sodium hydrogen carbonate (25 g, 0.298 mol) for 1 h and then filtered *in vacuo* at 3 Torr and 150°C for removal of low-boiling-point substances.

To a mixture of 2-allylphenol (30 g, 0.22 mol) and a platinum-alcoholate catalyst (0.0028 g), 158 g of the oil previously obtained was added at 90°C. Then, the mixture was heated for 2 h at 90–100°C, and the resulting product was extracted with dichloromethane, washed several times with 80% aqueous methanol for the removal of excess 2-allylphenol, and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* by heating to a temperature of 115°C, and an oily product was finally obtained.

According to NMR analysis, the product was identified as PDMS with an average of 38 chem-



Scheme 1

ically combined dimethylsiloxy and terminal phenol units. The content of the phenolic hydroxyl group (OH) was calculated to be 0.6515 mmol/g. From the measurement, the n_D value of the reactive PDMS was 1.422.

Preparation of the PC-PDMS Block Copolymer

A solution prepared by the dissolution of reactive PDMS (88.4 g) in dichloromethane (2 L), as well as 5.8 wt % aqueous sodium hydroxide (450 mL) and TEA (4.37 g, 43.2 mmol), was added to the PC oligomer solution (10 L; CF, 7.2 mol). The mixed solution was stirred at 300 rpm at room temperature for 1 h. Sodium dithionite (1.1 g, 6.3 mmol), BPA (547 g, 2.39 mol), a solution prepared by the dissolution of sodium hydroxide (335 g, 8.37

mmol) in water (5 L), and a solution prepared the dissolution of PTBP (86.1 g, 0.573 mol) in dichloromethane (10 L) were also added and stirred at 500 rpm for 2 h at 23°C. Afterward, dichloromethane (5 L) was added, and the solution was washed successively with water (5 L), 0.01M aqueous sodium hydroxide (5 L), 0.1M aqueous hydrochloric acid (5 L), and water (5 L). Then, the solvent was evaporated to obtain the PC-PDMS block copolymer in a flake form.

The resulting PC-PDMS block copolymer was dried for 12 h at 110°C and pelletized by an extruder at 280°C.

The resulting pelletized copolymer was dried for 12 h at 120°C and press-molded with mirror-finished aluminum sheets at 290°C, and the

Table I Preparation of PMMA Macromonomers^a

| Run | Name | $[I]_0/[M]_0$ (10^{-3}) | $[S]_0/[M]_0$ (10^{-2}) | Yield (%) | COOH ^b (mmol/g) | GPC ^c | | |
|-----|-------|--------------------------------|--------------------------------|--------------|-------------------------------|------------------|--------|-----------|
| | | | | | | M_n | M_w | M_w/M_n |
| 1-1 | Mac-1 | 7.00 | 5.91 | 41 | 0.7037 | 3,000 | 6,900 | 2.30 |
| 1-2 | Mac-2 | 7.00 | 1.95 | 37 | 0.2185 | 8,500 | 16,500 | 1.94 |

^a Reactions were carried out in THF. $[I] = [AIBN]$, $[S] = [TMA]$, $[M] = [MMA]$.

^b Calculated by titration with aqueous potassium hydroxide.

^c Calculated with the calibration curve for polystyrene.

Table II Syntheses and n_D Values of PC–PMMA Graft Copolymers

| Run | Feed | | | Graft Copolymer | | | |
|-----|--------------|--------------------------|-----------------------------|--|------------------|-----------|--------------------|
| | Macromonomer | COOH/CF (Molar Ratio) | PTBP ^a (wt %) | PMMA Content ^b (wt %) | GPC ^c | | |
| | | | | | M_w | M_w/M_n | n_D ^d |
| 2-1 | Mac-1 | 0.10 | 1.44 | 10.5 | 36,300 | 2.02 | 1.575 |
| 2-2 | Mac-2 | 0.10 | 1.44 | 21.6 | 38,000 | 1.95 | 1.564 |
| 2-3 | Mac-1 | 0.25 | 1.44 | 21.6 | 21,400 | 1.88 | 1.564 |
| 2-4 | Mac-2 | 0.25 | 1.44 | 37.9 | 24,600 | 2.03 | 1.545 |
| 2-5 | Mac-1 | 0.10 | 0.72 | 11.0 | 59,500 | 2.43 | 1.575 |
| 2-6 | Mac-2 | 0.10 | 0.72 | 19.9 | 56,600 | 2.33 | 1.566 |
| 2-7 | Mac-1 | 0.25 | 0.72 | 23.4 | 29,100 | 2.35 | 1.562 |
| 2-8 | Mac-2 | 0.25 | 0.72 | 34.9 | 27,000 | 2.11 | 1.549 |
| 2-9 | Mac-2 | 0.49 | 0.72 | 40.2 | 49,500 | 1.94 | 1.542 |

^a Ratio of PTBP feedstock to the total amount of BPA, PC oligomer (PCO), and PTBP feedstock.

^b Calculated with ¹H-NMR.

^c Calculated with the calibration curve for PC.

^d Measured by Abbe's refractometer.

molding so obtained was subjected to n_D measurements.

Preparation of the PC Copolymer and GF Composites

The PC copolymer and GF were pelletized at 300°C with a vented twin-screw extruder with a GF inlet downstream of the PC feeding hopper.

The resulting pellets were dried for 4 h at 120°C and press-molded with mirror-finished alu-

minum sheets at 300°C, and the obtained molding (2 mm thick) was subjected to haze testing.

Measurements

The molecular weight and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] for the macromonomer and PC–PMMA graft copolymer were determined by gel permeation chromatography (GPC; Waters 410, Tokyo, Japan) with polystyrene gel columns (Tosoh TSK gel GMH6, Tokyo, Japan) at 40°C with THF. The molecular weights of the macromonomer and PC–PMMA graft copolymer were calculated according to a standard procedure based on the universal calibration curves for polystyrene and PC, respectively.

The viscosity-average molecular weight (M_v) of the PC–PDMS block copolymer was obtained by the measurement of the viscosity of the polymer–dichloromethane solution with different concentrations at 20°C with an Ubbelohde viscometer and the subsequent derivation of the intrinsic viscosity $[\eta]$ by extrapolation and substitution into the following equation:¹

$$[\eta] = 1.23 \times 10^{-5} M_v^{0.83}$$

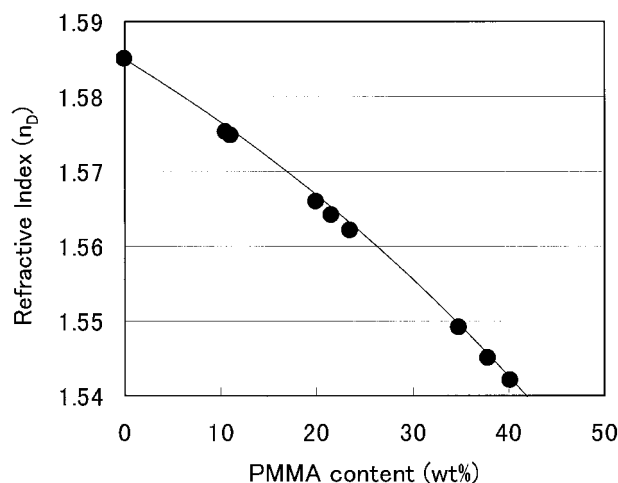
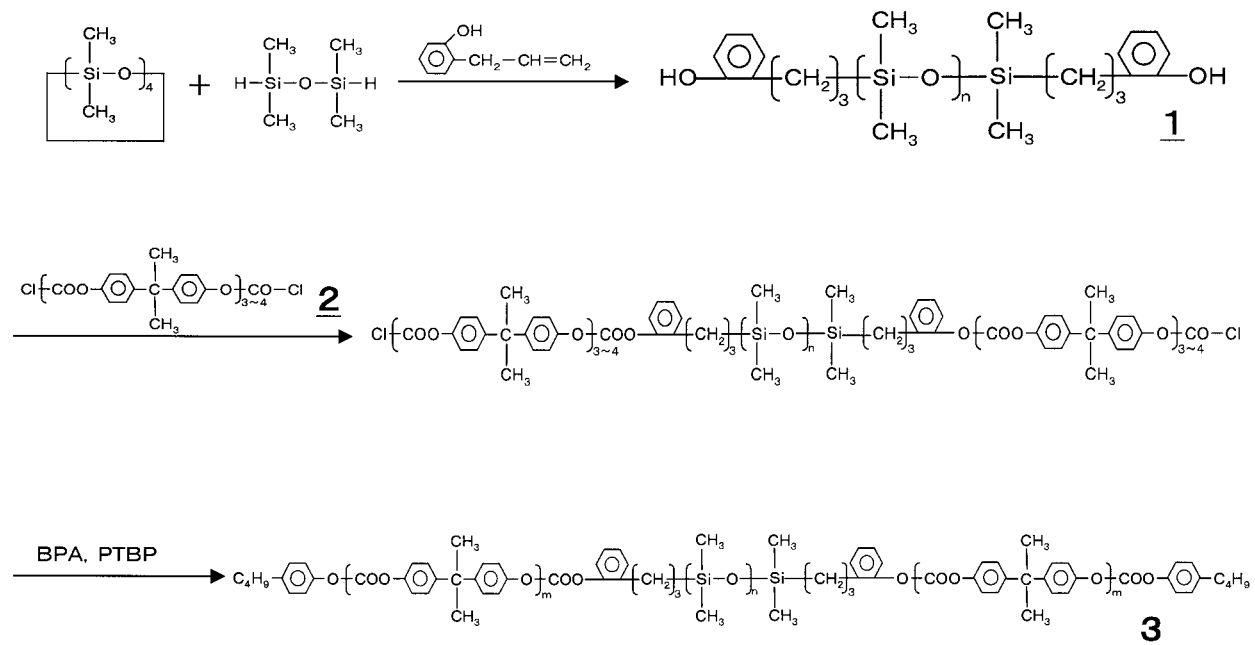


Figure 1 Relationship between the PMMA content and n_D .

The ¹H-NMR spectrum was recorded with a JEOL EX-400 NMR spectrometer (Tokyo, Japan)



Scheme 2

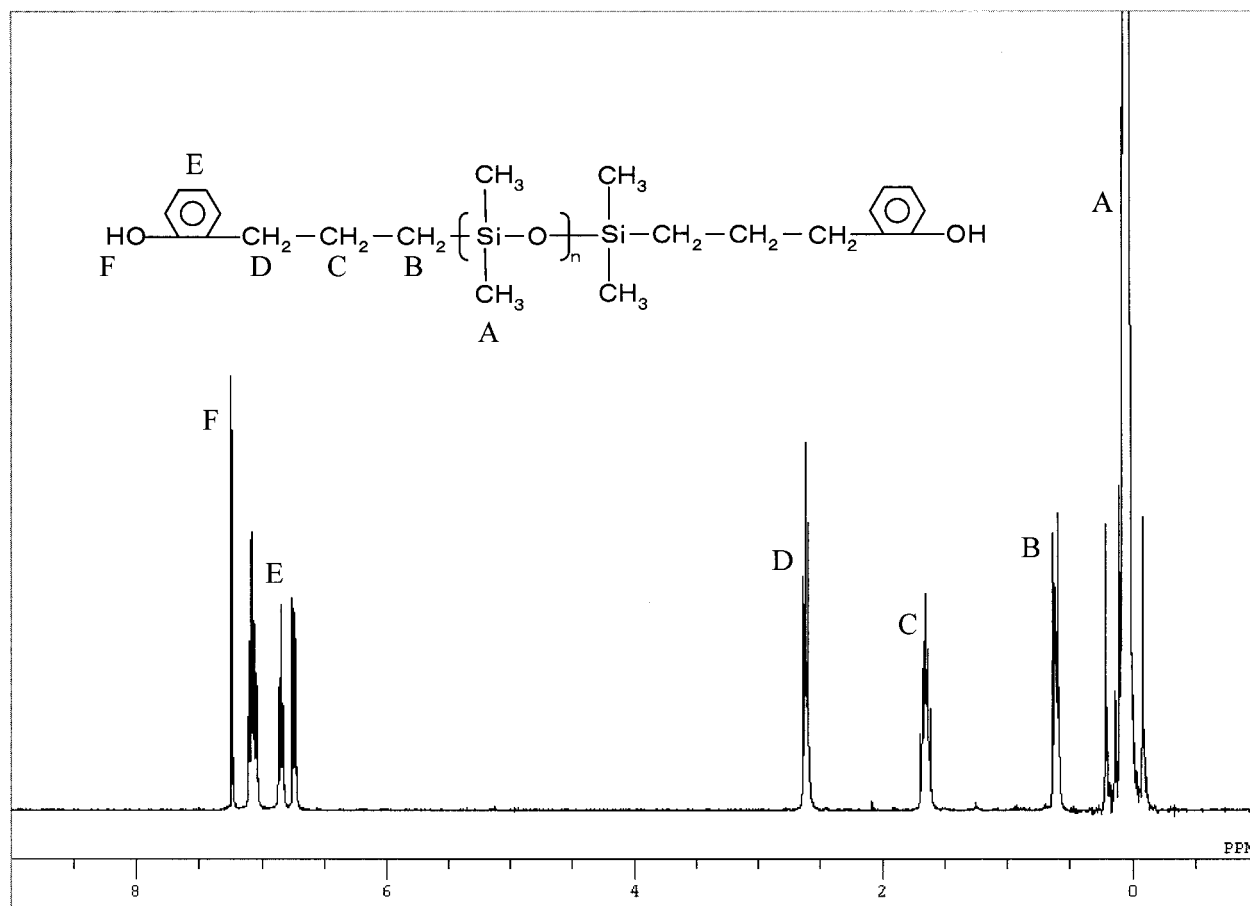
Figure 2 $^1\text{H-NMR}$ spectrum of the reactive PDMS in CDCl_3 .

Table III Syntheses and n_D Values of PC–PDMS Block Copolymers

| Run | Feed | | Block Copolymer | | |
|-----|------------------------|-----------------------------|-------------------------------------|--------|---------|
| | OH/CF (Molar Ratio) | PTBP ^a (wt %) | PDMS Content ^b (wt %) | M_v | n_D^c |
| 3-1 | 0.008 | 2.3 | 2.0 | 18,500 | 1.579 |
| 3-2 | 0.016 | 2.3 | 4.0 | 18,700 | 1.574 |
| 3-3 | 0.035 | 1.5 | 7.8 | 26,100 | 1.566 |
| 3-4 | 0.070 | 1.5 | 15.6 | 24,300 | 1.551 |
| 3-5 | 0.091 | 1.5 | 19.1 | 24,200 | 1.545 |

^a Ratio of PTBP feedstock to the total amount of BPA, PCO, and PTBP feedstock.

^b Calculated with ¹H-NMR.

^c Measured by Abbe's refractometer.

operating at 400.15 MHz. The prepared copolymer solution had a concentration of 70 mg/mL in CDCl₃.

n_D was measured with an Abbe's refractometer with a sodium lamp. The haze was measured in conformity with JIS K 7105.

RESULTS AND DISCUSSION

PC–PMMA Graft Copolymer

The preparation of the PC–PMMA graft copolymer was carried out according to Scheme 1. The dicarboxyl-terminated macromonomer (**1**) was prepared by the radical polymerization of MMA initiated by AIBN in the presence of TMA as a chain-transfer agent. The results are summarized in Table I. The PC oligomer with CF groups at the ends of the chain (**2**) was prepared by condensation of BPA and excess phosgene (1.4/1 phosgene/BPA) in aqueous sodium hydroxide. Because the number-average molecular weight (M_n) was 890, the degree of polymerization of the PC oligomer was estimated to be 3–4. The synthesis of the graft copolymer (**3**) was carried out as follows. The first step was the condensation of **1** and **2** in dichloromethane in the presence of TEA as an acid acceptor, giving the prepolymer with CF groups at the chain ends. Then, the interfacial polycondensation of BPA and the prepolymer, in the presence of TEA as a phase-transfer catalyst, led to **3**, which was washed with acetone for the removal of unreacted PMMA. The syntheses of **3** are summarized in Table II.

The reaction of the COOH and CF groups produced acylcarbonate, which underwent decarboxylation to give an ester.¹² This decarboxylation

was confirmed by the model reaction of succinic acid and phenyl chloroformate.⁸

The structure of **3** was characterized by IR and ¹H-NMR spectroscopy.⁸ The PMMA content of **3** was calculated from the integral ratio of the phenyl proton (7.2 ppm) of the PC unit to the methoxy proton of the PMMA unit (3.8 ppm).

The n_D value of the PC–PMMA graft copolymer is summarized in Table II. Figure 1 shows the relationship between the PMMA content and n_D . The n_D value of the graft copolymer decreased with the increasing PMMA content. Thus, it was anticipated that with the increasing PMMA content, the n_D value of the copolymer would decrease close to 1.489; that is, the n_D value of PMMA.¹³ It was presumed that, with a PMMA content of 38 wt %, the n_D value of the PC–PMMA graft copolymer was almost the same as that of E glass (1.545) and, with a PMMA content of 6 wt %, the same as that of ECR glass (1.579).

PC–PDMS Block Copolymer

The preparation of the PC–PDMS block copolymer was carried out according to Scheme 2. An insertion reaction of OMTS into TMDS and end-capping by 2-allylphenol led to reactive PDMS with phenolic hydroxyl groups at the ends of the chain (**1**). The degree of polymerization of **1** was controlled by the mixing ratio of OMTS to TMDS. The structure of **1** was characterized with ¹H-NMR spectroscopy. The ¹H-NMR spectrum of reactive PDMS is shown in Figure 2. The methyl protons appear at 0.1 ppm, the trimethylene protons appear at 0.6, 1.7, and 2.6 ppm, the aromatic protons appear at 6.7–7.1 ppm, and the phenolic hydroxyl protons appear at 7.25 ppm. The degree of polymerization was calculated to be 38 from the

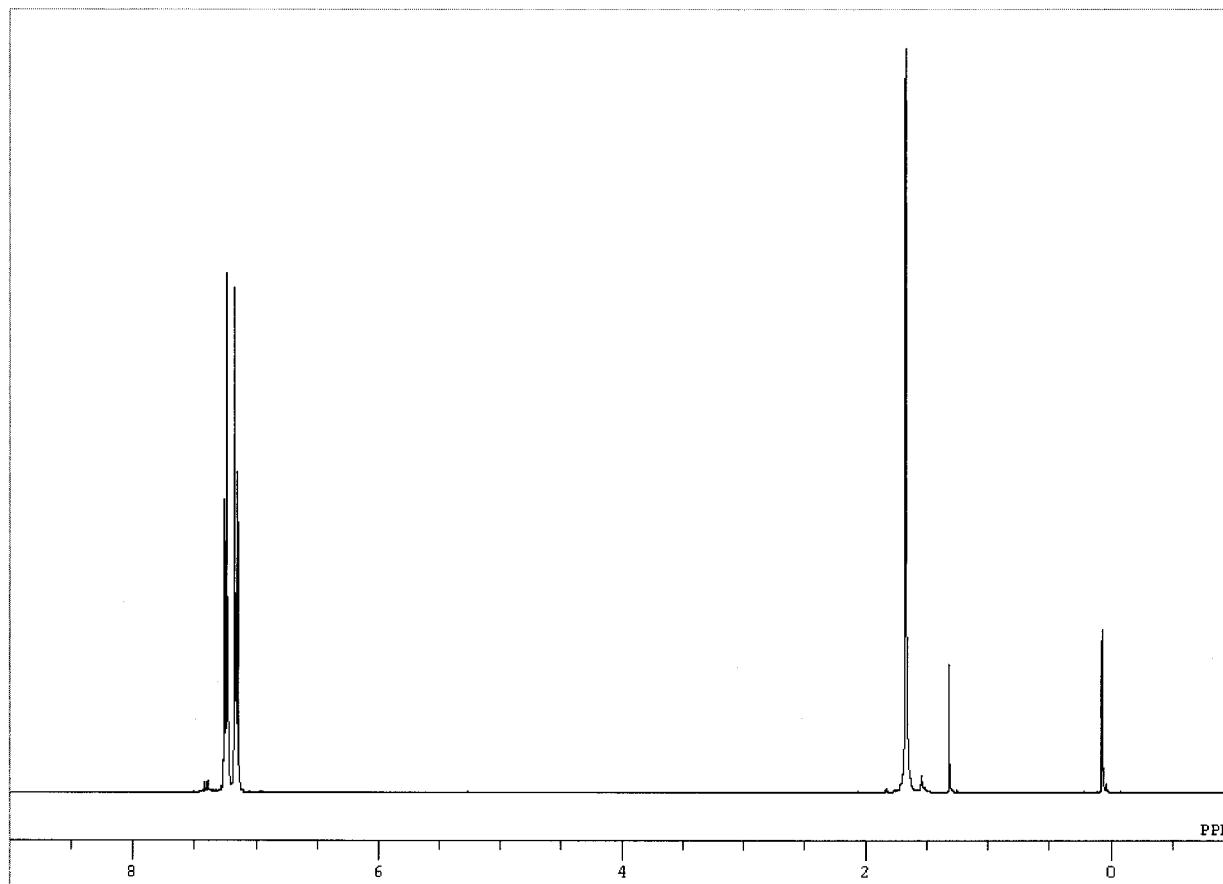


Figure 3 $^1\text{H-NMR}$ spectrum of the PC-PDMS block copolymer (Run 3-1) in CDCl_3 .

integral ratio of the methyl protons to the trimethylene protons.

The synthesis of the PC-PDMS block copolymer (**3**) was carried out as follows. The two-step method was used to prepare **3**; it was similar to that used for the PC-PMMA graft copolymer. The first step was the precondensation of **1** and the PC oligomer (**2**), giving the prepolymer with CF groups at the chain ends. The second step was the polycondensation of BPA and the prepolymer. The syntheses of **3** are summarized in Table III.

The structure of **3** was characterized with $^1\text{H-NMR}$ spectroscopy. The $^1\text{H-NMR}$ spectrum of the block copolymer (Run 3-1 in Table III) is shown in Figure 3. The aromatic protons of the PC unit appear at 7.2 ppm (d) and 7.3 ppm (d), and its methyl protons appear at 1.7 ppm. The signal observed at 0.1 ppm is assigned to the methyl protons of the PDMS unit. The *tert*-butyl protons of the terminal appear at 1.3 ppm. The PDMS content of **3** was calculated from the integral ratio of the methyl protons (1.7 ppm) of the PC unit to the methyl protons of the PDMS unit (0.1 ppm).

The n_D value of the PC-PDMS block copolymer is summarized in Table III. Figure 4 shows the relationship between the PDMS content and n_D . The n_D value of the graft copolymer decreased with the increasing PDMS content. Thus, it was

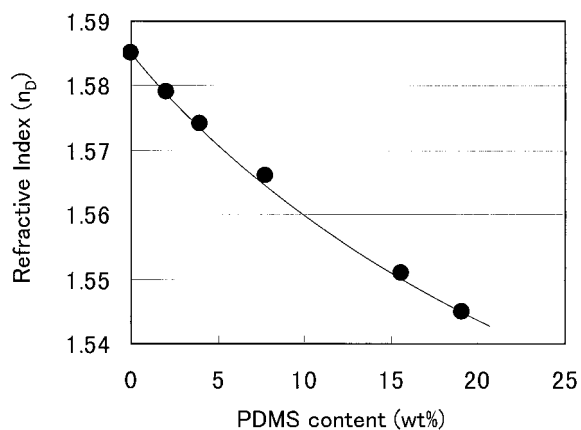


Figure 4 Relationship between the PDMS content and n_D .

Table IV Preparation and Transparency of GFPC

| Run | Polymer | | GF | | Δn_D | Haze ^a (%) |
|-----|-----------------|------------------|----------------|------------------|--------------|--------------------------|
| | Kind | Amount (wt %) | Kind | Amount (wt %) | | |
| 4-1 | Run 3-1 | 90 | ECR | 10 | 0.000 | 8 |
| 4-2 | PC ^b | 90 | ECR | 10 | 0.006 | 15 |
| 4-3 | PC | 90 | E ^c | 10 | 0.040 | 85 |
| 4-4 | Run 3-1 | 80 | ECR | 20 | 0.000 | 16 |
| 4-5 | PC | 80 | ECR | 20 | 0.006 | 29 |
| 4-6 | PC | 80 | E | 20 | 0.040 | 90 |
| 4-7 | PC | 100 | — | — | — | 3 |

^a Measured in conformity to JIS Z 7105.

^b Toughlon A2500 manufactured by Idemitsu Petrochemical Co., Ltd.

^c MA-409C manufactured by Asahi Fiber Glass Co., Ltd.

anticipated that with the increasing PMMA content, the n_D value of the copolymer would decrease close to 1.43, that is, the n_D value of PDMS.¹³ Presumably, with a PDMS content of 19 wt %, the n_D value of the PC–PDMS block copolymer was nearly the same as that of E glass (1.545) and, with a PDMS content of 2 wt %, the same as that of ECR glass (1.579).

Transparency of GFPC

With the PC–PDMS block copolymer, the transparency of GFPC was examined through the measurement of the haze. The results are summarized in Table IV. The combination of commercially available PC and E-GF ($\Delta n_D = 0.040$) gave a haze value of 85% with a GF content of 10% and a haze value of 90% with a GF content of 20%. With ECR-GF ($\Delta n_D = 0.006$) instead of E-GF, the haze values were 15% (GF content of 10%) and 29% (GF content of 20%). Thus, transparency was improved but was still not satisfactory. However, the combination of the PC–PDMS block copolymer (Run 3-1 in Table III) and ECR-GF ($\Delta n_D = 0$) led to haze values of 8 and 16% with GF contents of 10 and 20%, respectively. The transparency was more improved. However, the transparency of GFPC was still not equivalent to that of PC. This might have been due to the difference in Abbe's number (ν_D) between the resin and the GF. The ν_D value of the PC–PDMS block copolymer

(run 3-1 in Table III) was approximately 31, and that of ECR-GF was approximately 55. It seemed necessary to consider both n_D and ν_D to further improve the transparency of GFPCs.

REFERENCES

1. Schnell, H. *Chemistry and Physics of Polycarbonate*; Interscience: New York, 1964.
2. Freitag, D.; Fengler, G.; Morbitzer, L. *Angew Chem Int Ed Engl* 1991, 30, 1598.
3. Kawashima, S.; Kitsunozuka, A. *Reinf Plast* 1991, 36, 277.
4. Chu, J.; Sullivan, J. L. *Polym Compos* 1996, 17, 556.
5. Henshaw, J. M.; Owens, A. D.; Houston, D. Q.; Smith, I. T.; Cook, T. J. *Thermoplast Compos Mater* 1994, 7, 14.
6. Parikh, S. S. *Prepr Annu Conf Reinf Plast Compos Inst* 1984, 39(13B), 1.
7. Parikh, S. S.; Leslie, D. J. *Prepr Annu Conf Reinf Plast Compos Inst* 1983, 38(15C), 1.
8. Okamoto, M. *J Appl Polym Sci* 2001, 80, 2670.
9. Yamashita, Y.; Chujo, Y.; Kobayashi, H.; Kawakami, Y. *Polym Bull* 1981, 5, 361.
10. Chujo, Y.; Tatsuda, T.; Yamashita, Y. *Polym Bull* 1982, 8, 239.
11. Krantz, K. W. *Pat. UK 1175266* (1969).
12. Riffle, J. S.; Freelin, R. G.; Banthia, A. K.; McGrath, J. E. *J Macromol Sci Chem* 1981, 15, 967.
13. Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999; p V1/574.